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Synthesis of lamellar Shape $KZnPO_4$ and Its Standard Molar Enthalpies of Formation

Sheng-fu Wu[a],Shao-mei Ma[b], Zeng-wei Huang [b], An-ping Liao[b] and Ai-qun Yuan[b*]

[a]*College of pre-education, Guangxi University for Nationalities, Nanning 530006, Guangxi, People's Republic of China*

[b]*College of Chemistry and Ecology Engineering, Guangxi University for Nationalities; key laboratory of new technology of chemical and biological transformation processes,Nanning 530006, Guangxi, People's Republic of China*

Abstract

$KZnPO_4$ was synthesized by solid-state reaction at low temperature and characterized by X-Ray Diffraction, Scanning electron microscope and elemental analysis. Thermochemical study was performed with an isoperibol solution calorimeter. Based on Hess's law, thermochemical cycles were designed to determine the dissolution enthalpies of reactants and products using a solution-reaction isoperibol calorimeter at 298.15 K, and the molar reaction enthalpies were calculated on the basis of above dissolution enthalpies. The results show that the obtained product is layered shape $KZnPO_4$. The standard molar formation enthalpy of the $KZnPO_4$ at 298.15 K is obtained.

Keywords: Potassium zinc phosphate; Solid-state reaction at low temperature; Standard molar enthalpy of formation

1. Introduction

Layered phosphates are of great interest with respect to their extensive use in heterogeneous catalysts [1.2]. It is known that some of them can undergo ion exchange and reversible hydration in the same way as zeolites. Like many other phosphates, potassium zinc phosphate has layered structure, and has attracted extensive attention for its potential as a catalyst. Wu et al [3] has investigated synthesis of micronutrient fertilizer potassium zinc phosphate. Chen et al [4] found that potassium zinc phosphate, even without any

*Corresponding author, Tel: +86 771 6410889; Fax: +86 771 3262396

E-mail address: aiqunyuan1999@yahoo.com.cn, aiqunyuan1999@sina.com. (A.Q. Yuan)

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load, is also a good catalyst for Knoevenagel condensation reaction or Michael addition reaction. Usually, metal phosphate with layered structure can be obtained by hydro-thermal or solvent-thermal method or solid-state reaction. Anandalakshmi et al [5] reported the single crystals structural of zinc potassium phosphate hexahyate $ZnKPO_4 \cdot 6H_2O$ synthesized by equimolar aqueous solution of potassium dihydrogen phosphate and zinc sulphate. Sambasiva Rao et al [6] studied the electron paramagnetic resonance of zinc potassium phosphate hexahyate. Although there have been synthesis and performance reports on this compound, to our knowledge, thermodynamic properties of these compounds are sparse.

In previous studies, we have synthesized some zinc phosphate double-salts by solid-state reaction at room temperature. Then, we developed a new solid-state synthetic route for the preparation of layered phosphates $NH_4MPO_4 \cdot H_2O$(M=Mn^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+})[7,8]. Based on the previous studies, we have prepared $KZnPO_4$ and investigated their thermochemical properties.

2. Experimental

2.1Reagents

All the chemical regents were analytical grade. KCl with purity higher than 99.99 % was dried in a vacuum oven for 6 h at 120 ℃.

2.2Preparation of $KZnPO_4$

$K_3PO_4 \cdot 3H_2O$ and $ZnSO_4 \cdot 7H_2O$ were mixed together with molar ratio of 1:1. This mixture was ground for 60 min by addition of a non-ion surfactant PEG-400 and left in an oven at 40 ºC for 36 h. The white powder obtained was washed with water until no SO_4^{2-} was detected in filtrate, Then washed with ethanol and dried at 110 ºC for 5 h.

2.3 Characterization

X-ray powder diffraction (XRD) was carried out by D/max-2500V diffractometer (Japan) utilizing Cu-Kα radiation (λ=0.154056 nm) at 40 kV/200 mA. The diffraction patterns were measured in the range of 5º<2θ<50º. The particle shape of SEM picture, EDS and composition were determined by X-650 scanning Electronic Microscope (Japan), GENESIS Energy Dispersive Spectrometer (EDAX Company, USA) and elemental analysis.

2.4Calorimeter and calibration

The calorimeter [7,8] was calibrated by determining the dissolution enthalpy of KCl (calorimetric primary standard) in water at 298.15 K .The mean dissolution enthalpy was 17.47 ± 0.25 $KJ \cdot mol^{-1}$ in agreement with the value of 17.54 ± 0.01 $KJ \cdot mol^{-1}$ of Reference [9]. The uncertainty and the inaccuracy of the experimental results were within ±0.3 % compared with the recommended reference data.

3. Result and discussion

3.1Identification of synthetic sample

Metal and phosphorous contents of the titled compounds are shown in Table 1. From this table we can found the determined results are in good agreement with the calculated values of these two phosphates respectively. XRD pattern of the product was showed in Figure 1, which matches the standard XRD data for $KZnPO_4$ of JCPDF81-1034. The XRD data indexed as a hexagonal system and space group $P6_3$ (173), a=b=18.155 Å, c=8.504, V=2427.4 $Å^3$, Z=24, Dc=3.250 $g \cdot cm^{-3}$. Scanning EM picture (See Figure 1 shows $KZnPO_4$ has a lamellar shape particle, and they are micro or submicron particles. The energy

dispersive spectrometer and its analysis results are shown in Figure 2. From the mass fraction of potassium, zinc and phosphorus 13.88%, 23.16% and 11.05% (including carbon 15.64%from conductive adhesive used in determination), the molar ratio of these elements can be calculated as K: Zn: P=1:1:1, which Is corresponding to molecular formula of $KZnPO_4$.

Table 1 Elemental analysis results of $KZnPO_4$

$KZnPO_4$	Determination			Calculation		
	Zn/%	P/%	K/%	Zn/%	P/%	K/%
Results	32.68	15.61	19.51	32.66	15.58	19.60

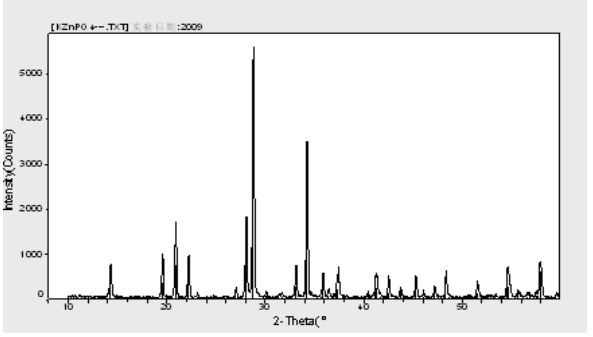

Fig. 1 XRD pattern of $KZnPO_4$

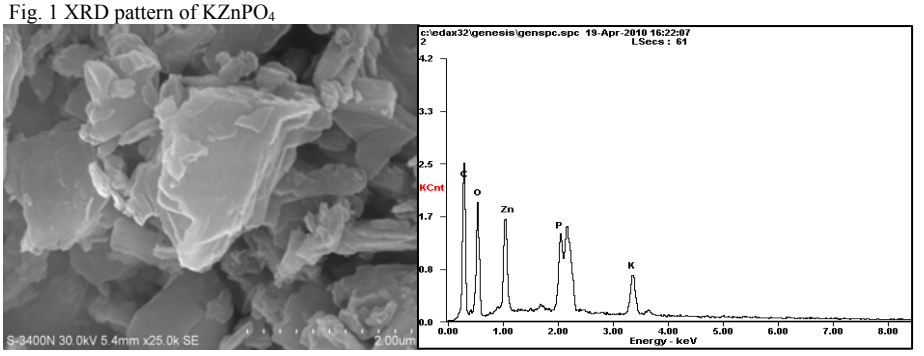

Fig. 2 SEM picture and EDS analysis of $KZnPO_4$

3.2Calorimetric experiment

To obtain the standard enthalpy of formation for $KZnPO_4$, this compound can be regarded as the product of the following reaction, and the thermochemical cycle was designed as shown in Figure 3. If the dissolution enthalpies of reactants ($\Delta_sH_1^{\ominus}$, $\Delta_sH_2^{\ominus}$) and products ($\Delta_sH_3^{\ominus}$, $\Delta_sH_4^{\ominus}$), and with the aid of auxiliary data, the $\Delta_rH_m^{\ominus}$ and $\Delta_fH_m^{\ominus}$ of $KZnPO_4$can be obtained.

3.2.1 Determination of $\Delta_sH_1^{\ominus}$, $\Delta_sH_2^{\ominus}$, $\Delta_sH_3^{\ominus}$, $\Delta_sH_4^{\ominus}$

Molar dissolution enthalpy of reactants and products of $KZnPO_4$ in 4mol·L^1HCl is showed in Table 2 and Table 3, respectively. These results were calculated from the average of five experiments.

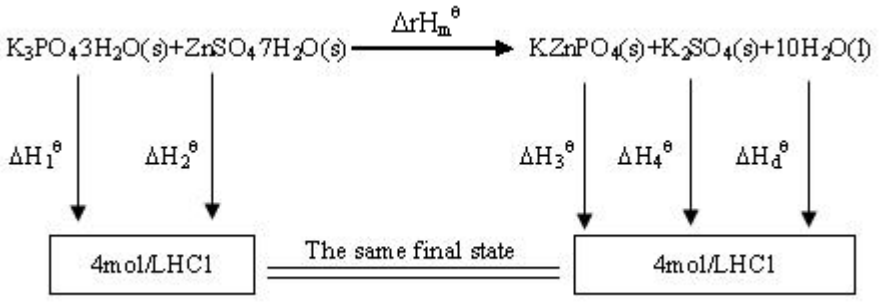

Fig.3 Scheme of the thermochemical cycle of $KZnPO_4$

($\Delta_r H_m^{\ominus}=\Delta_s H_1^{\ominus}+\Delta_s H_2^{\ominus}-\Delta_s H_3^{\ominus}-\Delta_s H_4^{\ominus}-\Delta_s H_d^{\ominus}$, Where: $\Delta_s H_1^{\ominus}$, $\Delta_s H_2^{\ominus}$ is the dissolution enthalpies of two reactants in 4mol·L^{-1} HCl; $\Delta_s H_3^{\ominus}$, $\Delta_s H_4^{\ominus}$ is the dissolution enthalpies of two of the products in 4 mol·L^{-1} HCl; $\Delta H_d^{\ominus}$ is the dilution enthalpy of water in 4 mol·L^{-1} HCl; $\Delta_r H_m^{\ominus}$ is the enthalpy value for the designed reaction.

Table2 $\Delta_s H_1^{\ominus}$ and $\Delta_s H_2^{\ominus}$ of thermochemical cycle of $KZnPO_4$

No	Mass/g $K_3PO_4{\cdot}3H_2O$(s)	Q /J	$\Delta_s H_1^{\ominus}$ /kJ·mol^{-1}	Mass/g $ZnSO_4{\cdot}7H_2O$(s)	Q /J	$\Delta_s H_2^{\ominus}$ /kJ·mol^{-1}
1	0.3995	-82.9172	-55.2781	0.4313	96.8133	64.5435
2	0.3995	-83.1281	-55.4188	0.4313	96.6991	64.4660
3	0.3995	-84.5360	-56.3574	0.4313	96.8014	64.5343
4	0.3995	-82.6724	-55.1150	0.4313	96.4658	64.3105
5	0.3995	-83.4745	-55.6497	0.4313	97.3157	64.8771
Ave.			- 55.56±0.49			64.55±0. 21

Table3 $\Delta_s H_3^{\ominus}$ and $\Delta_s H_4^{\ominus}$ of thermochemical cycle of $KZnPO_4$

No	Mass/g $KZnPO_4$(s)	Q /J	$\Delta_s H_3^{\ominus}$ /kJ·mol^{-1}	Mass/g K_2SO_4(s)	Q /J	$\Delta_s H_4^{\ominus}$ /kJ·mol^{-1}
1	0.2992	-19.2051	-12.8034	0.2614	63.0954	42.0596
2	0.1496	-9.1208	-12.1610	0.2614	63.1835	42.1223
3	0.2992	-18.0107	-12.0071	0.2614	63.4532	42.3021
4	0.2992	-19.3023	-12.8682	0.2614	63.4988	42.3326
5	0.2992	-18.8917	-12.5944	0.2614	64.0228	42.6818
Ave.			-12.49±0.39			42.30±0.24

3.2.2Calculation of the standard molar formation enthalpies for $K_3PO_4{\cdot}3H_2O$

With the aid of the auxiliary data in Table 4, the molar standard formation enthalpy of $K_3PO_4{\cdot}3H_2O$ could be calculated from the dissolution enthalpies of these compounds through the designed equation (1). The results have been listed in Table 5.

$$K_3PO_4{\cdot}3H_2O(s)+H_2O(l) = 3K^+(aq)+PO_4^{3-}(aq)+4\ H_2O(l) \quad (1)$$

$$\Delta_{sol}H_m^{\theta}[K_3PO_4{\cdot}3H_2O(s)]=3\Delta_f H_m^{\theta}[K^+(aq)]+\Delta_f H_m^{\theta}[PO_4^{3-}(aq)]+3\Delta_f H_m^{\theta}[H_2O(l)]-\Delta_f H_m^{\theta}[K_3PO_4{\cdot}3H_2O(s)]$$

So, $\Delta_f H_m^{\theta}(K_3PO_4{\cdot}3H_2O(s))$= -2880.99±0.18 kJ·$mol^{-1}$

Table 4 Ancillary data of standard enthalpies of formation at 298.15 K

Index	$\Delta_f H_m^{\ominus}$ / kJ·mol^{-1}	References
$ZnSO_4$·7H2O,s	-3077.75	[11]
K^+,aq	-252.14	[12]
PO_4^{3-},aq	-1277.40	[12]
K_2SO_4,s	-1437.80	[11]
H_2O, l	-285.830±0.042	[12]

Table5 Dissolution enthalpies of $K_3PO_4 3H_2O$(s)in 100 mL 4 mol·L^{-1} HCl at 298.15 K

NO.	w($K_3PO_4 3H_2O$(s))/g	Q/J	$\Delta_{sol}H_m^{\theta}$/kJ.mol^{-1}
1	0.7990	-30.8578	-10.2860
2	0.7990	-31.0795	-10.3598
3	0.7990	-31.4002	-10.4667
4	0.7990	-31.3425	-10.4475
5	0.7990	-30.0608	-10.0203
Ave.			-10.32±0.18

3.2.3 Calculation of $\Delta H_d^{\ominus}$, $\Delta_r H_m^{\ominus}$ and $\Delta_f H_m^{\ominus}$

According to the literature 11, the dilution enthalpies of 10 mmol water in 100 mL 4 mol·L^1 HCl at 298.15 K can be calculated as:

$$\Delta H_{d\ (4.000\rightarrow 3.9892)} = \Delta H_{d\ (4.000\rightarrow 0)} - \Delta H_{d\ (3.992454\rightarrow 0)} = -0.0098\ \text{kJ·mol}^{-1}$$

Based on the data already obtained, the molar enthalpy of reaction was calculated. From these values and using various ancillary data (See Table 6), the standard molar enthalpies of formation can also be calculated.

$$\Delta r H_m^{\theta} = \Delta H_1^{\theta} + \Delta H_2^{\theta} - \Delta H_3^{\theta} - \Delta H_4^{\theta} - \Delta H_d^{\theta} = -20.83 \pm 0.70\ \text{kJ/mol}$$

$$\Delta_f H_m^{\theta}\ (KZnPO_4,s) = -1683.47 \pm 0.72\ \text{kJ/mol}$$

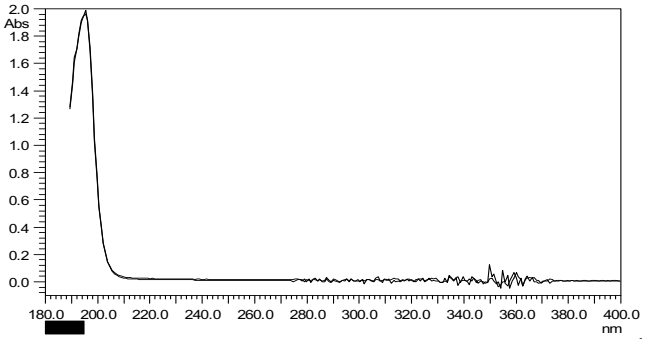

Fig. 4 Ultraviolet absorption spectrometry of reactions and products of $KZnPO_4$ in 4 mol·L^{-1}HCl

3.2.4 Determine of final state of the reactions

The UV-Vis spectra (see Figure4) of the final solution of the reactants and the products could also be used to determine whether they have the same thermodynamic state. It can be seen the ultraviolet absorption of solution obtained by dissolving reactant or the product in 100 mL 4 mol·L^{-1} HCl completely overlaps each other. Both conductivity values and refractive indexes after 500 times diluted are almost the same. All these results show both reactant and the product have the same dissolved state to ensure realization of the thermochemistry cycle. Therefore, we believed these standard enthalpies determined by solution-reaction calorimetry are reliable.

4. Conclusions

Solid-state reaction at low temperature can be used to prepare $KZnPO_4$ with layered structure. Standard molar formation enthalpy of $KZnPO_4$ at 298.15 K is $\Delta_f H_m^{\ominus}[KZnPO_4,s]$ =-1683.46±0.72 kJ·mol^{-1}.

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